

UK Patent Application (19) GB (11) 2 132 623 A

(21) Application No 8333324

(22) Date of filing 14 Dec 1983

(30) Priority data

(31) 450089

(32) 15 Dec 1982

(33) United States of America (US)

(43) Application published

11 Jul 1984

(51) INT CL³

C09K 3/34 C08F 20/36

(52) Domestic classification

C3P DG

C4X 12

U1S 1387 1574 3071 C3P

C4X

(56) Documents cited

CA 95 187807v

CA 94 192828m

CA 94 157412z

CA 92 7071g

CA 91 202468y

CA 89 180400z

CA 88 43801x

(58) Field of search

C3P

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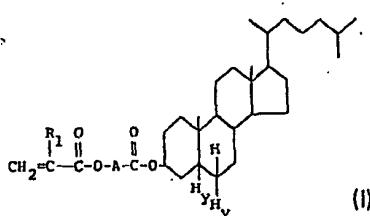
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(54) Polymeric liquid crystal films

(57) New polymeric cholesteric liquid crystal films are obtained by photopolymerisation of one or more monomers of formula I



wherein R₁ is H or CH₃; A is —R₂—, —R₃O—, or —R₄O—; R₂ is alkylene having 3—14 methylene or alkyl-substituted methylene groups; R₃ is alkylene having 2—14 methylene or alkyl-substituted methylene groups; R₄ is an alkylene ether, diether or

triether having a total of 3—14 carbon atoms in the alkylene linkages, provided that the alkylene linkage adjacent the carbonate moiety has at least two carbon atoms; the two H's are both H or together form an additional 5,6-bond.

The film is made from a mixture of (i) the monomer(s) of formula I, (ii) a photoinitiator, optionally (iii) a cross-linking agent, and optionally (iv) a further compound which is mesogenic and/or polymerisable e.g. 2-methyl-1,4-phenylene bis(4'-hexyloxybenzoate); cholesterolester carbonate; p-methoxyphenyl p-(6-methacryloyloxy)benzoate; cholesterolester 11-methacrylamide undecanoate.

The films have fixed optical characteristics, e.g. temperature-insensitive colours, and reflect specific wavelengths of light from the near u.v. into the i.r.

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SPECIFICATION
Polymeric liquid crystals

The present invention relates to liquid crystals and more particularly to polymeric liquid crystals which have fixed optical characteristics.

5 The existence of liquid crystalline materials has been recognized since the late 1800's. The terms "liquid crystal" and "mesogen" refer to a number of states of matter which lie between solid crystals and isotropic liquids, the latter being randomly ordered. Liquid crystalline materials possess some structural characteristics of crystals, yet they may be viscous or quite mobile liquids.

10 The varying degrees of order which are possessed by liquid crystals give rise to three distinct types of structures called mesophases. A liquid crystal, when in the crystalline state, has a three-dimensional uniform structure with orientational and positional order. As the crystal is heated, it may initially lose one dimension of its positional order. This is referred to as the smectic mesophase, a phase in which the liquid crystal retains the orientational order of the crystalline state, as well as two-directional positional order.

15 With further heating, the liquid crystal can convert to the nematic mesophase. In this phase, the remaining positional order is lost and the liquid crystalline material retains only the one-directional orientational order of the crystalline state. The molecular order of nematic mesophases is characterized by orientation of the molecules along an axis which coincides with the long axis of the molecules. The centers of gravity of the molecules are arranged randomly so that no positional long-range order exists.

20 In the cholesteric mesophase, the molecular order is characterized by orientation of the molecules along an axis which coincides with the long molecular axis as in a nematic phase; however, the axis changes direction in a continuous manner along a second axis perpendicular to the first. For this reason, cholesteric mesophases are often referred to as twisted nematic mesophases. Optical activity is necessary for a mesogenic material to form a cholesteric mesophase.

25 The term "cholesteric" is primarily of historical significance because the first-discovered liquid crystalline material which exhibited a cholesteric mesophase was cholesteryl benzoate. It has long been recognized, however, that the presence of the cholesterol moiety is not required, and that non-cholesterol derivatives may also exhibit a cholesteric mesophase.

30 Substantial interest has been shown in liquid crystalline materials which exhibit cholesteric mesophases because these materials exhibit unique optical properties such as selective reflection of visible light to produce iridescent colors, as well as circular dichroism. Thus, for example, U.S. Patent 3,720,623 discloses mixtures of cholesteric and nematic liquid crystals which are useful in temperature-sensitive visual displays; U.S. Patent 3,766,061 discloses decorative films comprising solid materials which are proportioned such that the composition demonstrates cholesteric properties; 35 U.S. Patent 3,923,685 discloses cholesteric materials which convert to the nematic state upon exposure to an electric field; and U.S. Patent 3,931,041 discloses combinations of nematic and potentially cholesteric material which are useful in imaging and display devices.

40 Although the colored images produced using cholesteric material are quite useful, most such images are not permanent. Accordingly, there has been substantial interest in preparing cholesteric materials in which the color can be fixed. Thus, U.S. Patent 3,766,061, which was referred to above, discloses decorative films in which the color is fixed by cooling. In addition, U.S. Patent 4,239,435 discloses a polymeric liquid crystal in which the color is fixed by lowering the temperature of the polymer below the glass transition temperature, thereby fixing the polymer in the solid state.

45 The use of temperature changes to fix the color is not always practical, however, and there has been interest in developing cholesteric materials whose color can be fixed by other means, such as by photopolymerization, whereby the resulting fixed color is temperature insensitive. The applicants are aware of only one such polymer. This was reported by a group of Japanese workers who disclosed that poly(gammabutyl-L-glutamate) in trimethylene glycol dimethacrylate could be photopolymerized to fix the color such that it was temperature insensitive.

50 Accordingly, one objective of the present invention is to provide polymeric cholesteric liquid crystalline materials having fixed, essentially temperature-insensitive colors.

Yet another objective of the present invention is to provide combinations of monomeric compounds which provide variable optical responses over a variety of temperature ranges.

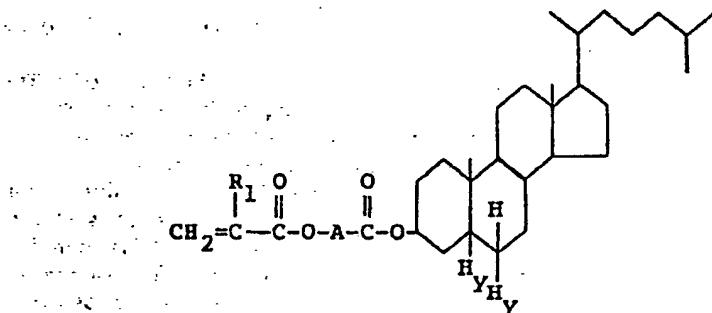
55 Yet another objective of the present invention is to provide polymeric films having fixed colors which are useful in a variety of optical devices.

These and other objectives of the present invention will become apparent from the detailed description of preferred embodiments which follow.

60 The present invention concerns novel cholesteric liquid crystalline monomers and combinations thereof with materials that will support formation of a mixture which demonstrates cholesteric liquid crystalline properties. These materials may be formed as films, heated or cooled to a desired temperature to cause the cholesteric film to exhibit a desired optical response, and photopolymerized to essentially fix the optical characteristics of the resulting polymer.

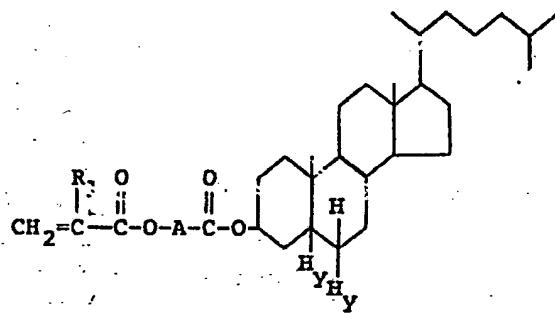
In one embodiment the present invention comprises a composition suitable to provide a

polymeric film having fixed optical properties, said composition comprising a photopolymerizable monomer having the structure



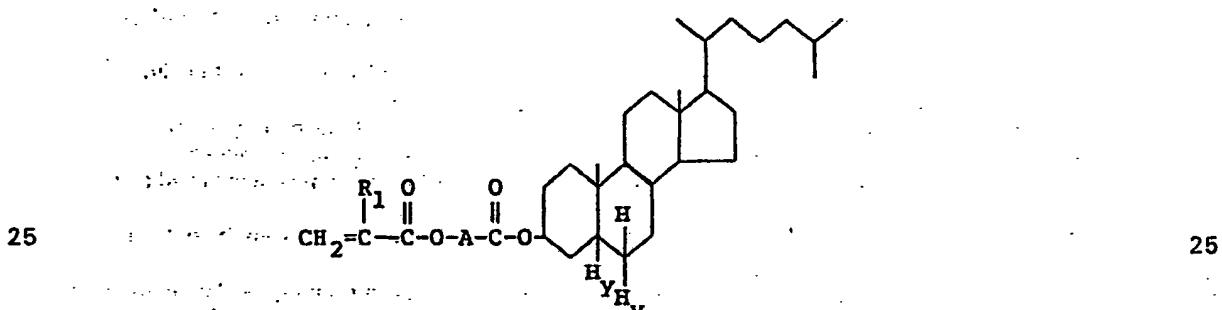
5 where $R_1=H$ or CH_3 , $A=R_2$, R_3O , or R_4O , R_2 =an alkylene chain having 3—14 methylene or lower alkyl-substituted methylene groups, R_3 =an alkylene chain having from 2—14 methylene or lower alkyl-substituted methylene groups, R_4 =an alkylene ether, diether or triether having a total of from 3—14 carbon atoms in the alkylene linkages, the alkylene linkages being branched or unbranched, any branches containing up to 4 carbon atoms, provided that the terminal alkylene linkage adjacent to the carbonate moiety comprises not less than two carbon atoms and $y=0$ or 1; and a 10 suitable photoinitiator.

In a second embodiment, the present invention comprises a polymeric film having a fixed optical response, said film being obtained by photopolymerizing a composition comprising a photopolymerizable monomer having the structure



15 where $R_1=H$ or CH_3 , $A=R_2$, R_3O , or R_4O , R_2 =an alkylene chain having from 3—14 methylene or lower alkyl-substituted methylene groups, R_3 =an alkylene chain having from 2—14 methylene or lower alkyl-substituted methylene groups, R_4 =an alkylene ether, diether or triether having a total of from 3—14 carbon atoms in the alkylene linkages, which may be branched or unbranched, any branch containing up to 4 carbon atoms, provided that the terminal alkylene linkage adjacent to the carbonate moiety comprises not less than two carbon atoms and $y=0$ or 1; and a suitable photoinitiator.

In a third embodiment the present invention comprises a process for preparing films comprising polymeric liquid crystalline materials having a fixed optical response, said process comprising the steps of preparing a film comprising a photopolymerizable monomer having the structure



25 where $R_1=H$ or CH_3 , $A=R_2$, R_3O , or R_4O , R_2 =an alkylene chain having from 3—14 methylene or lower alkyl-substituted methylene groups, R_3 =an alkylene chain having from 2—14 methylene groups, R_4 =an alkylene ether, diether or triether having a total of from 3—14 carbon atoms

in the alkylene linkages, which linkages may be branched or unbranched, any branch containing up to 4 carbon atoms, provided that the terminal alkylene linkage adjacent to the carbonate moiety comprises not less than two carbon atoms, and $y=0$ or 1; and a suitable photoinitiator; aligning said film; adjusting the temperature of said film to obtain a desired optical response; and photopolymerizing said film.

The cholesterol derivatives which may be used to practice the present invention are cholesterol (where $y=0$) and 5,6-dihydrocholesterol (where $y=1$). In addition, a number of options are available in the 3-position side chain. Thus, the polymerizable moiety of the side chain can comprise an acrylate or methacrylate moiety which is bridged to an ester or carbonate linkage. Where an ester linkage is present, the bridge will comprise an alkyl chain comprising from 3—14 methylene or lower alkyl-substituted methylene groups. Lower alkyl as used herein means an alkyl group comprising from 1—4 carbon atoms. The methacrylate esters, where R_1 and CH_3 and n (where n represents the number of carbon atoms in the methylene chain)=5, 10 and 14, have been reported in the Russian literature; however, these esters were prepared for use in solution polymerization reactions and there was no appreciation of their utility for preparing photopolymerized films as disclosed herein.

On the other hand, where a carbonate linkage is present, the bridge may be more complex. Thus, it may comprise from 2—14 methylene or lower alkyl-substituted methylene groups, or an alkylene ether, diether or triether having a total of from 3—14 carbon atoms in the alkylene linkages, the alkylene linkages being branched or unbranched, any branch containing up to 4 carbon atoms, provided that the terminal alkylene linkage adjacent to the carbonate moiety comprises not less than two carbon atoms. Examples of ether moieties which may be utilized in practicing the present invention are those which are analogous to ethylene glycol, diethylene glycol, triethylene glycol, tetramethylene glycol, 3,3'-oxybis-1-propanol, 4,4'-oxybis-1-butanol, and 1,1'-oxybis-2-propanol.

When in the pure state the above-described compounds are somewhat difficult to work with because they tend to crystallize inopportune. Furthermore, it is difficult to obtain colored polymers from the pure monomers because the majority of them will show either no colored cholesteric mesophase, or a very narrow colored cholesteric mesophase. Therefore, the pure compounds of the present invention are limited in their ability to produce polymeric films having desirable optical responses.

Surprisingly, it has been discovered that these limitations may be overcome and that colored and uncolored films comprising a compound described above and either another compound described above or a second material which is suitable to permit formation of a film that exhibits cholesteric liquid crystalline properties, can be prepared and photopolymerized in the presence of a suitable photoinitiator, thereby giving films having fixed optical characteristics. If the film is colored, the fixed color will preferably be substantially the same as the color of the unpolymerized film; however, in certain instances, it may be desirable to obtain a polymerized film having a fixed color which differs from that of the unpolymerized film. Thus, all such possibilities are contemplated by the present invention. Details relating to the preparation of the novel compounds used herein are set forth in our copending application No. 83—33323 the contents of which are hereby incorporated by reference.

A preferred method of practicing the present invention involves the preparation of a film which exhibits a desired optical characteristic at a specific temperature. For colored films, this has been conveniently achieved, for example, by preparing a mixture of the materials which provide the cholesteric film and the photoinitiator and, optionally, a crosslinking agent; heating the mixture to obtain a viscous liquid; spreading and aligning the liquid between glass plates; submerging the plates in a thermostatic water bath; and adjusting the temperature to obtain a desired color. For uncolored films, the optical characteristics must be determined spectrophotometrically. The film is then irradiated with a suitable radiation source, such as a mercury lamp. The polymeric films thus obtained can remain substantially unchanged even when exposed to high temperatures for several weeks, depending on the character of the second component as discussed in more detail below.

Examples of photoinitiators which will be useful to practice the present invention are benzophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxyacetophenone, 2-benzoyl-oxyacetophenone, 2-chlorothioxanthone and 2-hydroxycyclohexyl phenyl ketone, all of said compounds being mentioned by way of illustration and not limitation.

Examples of optional cross-linking agents which will be useful to practice the present invention are trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, ethyleneglycol diacrylate, ethyleneglycol dimethacrylate, di- and triethyleneglycol diacrylate and dimethacrylate, 1,6-hexanediol diacrylate and dimethylacrylate, 1,4-butanediol diacrylate and dimethacrylate, similarly substituted acrylamides and methacrylamides, and many others, said examples similarly being provided by way of illustration and not limitation.

A wide variety of combinations may be made to produce films having different optical characteristics, and these will be largely a matter of choice to the artisan. Nevertheless, several generalizations can be made regarding combinations of the novel monomeric compounds as described herein.

First, combinations of similar monomers will give films which exhibit cholesteric mesophases over a temperature range which is comparable to that of the individual monomers. For example, if an

acrylate/methacrylate pair of cholesterol derivatives is prepared where $y=0$ and $A=-(CH_2)_{10}-$, the methacrylate ($R_1=CH_3$) exhibits a color range (monotropic only) at $55.8-55.3^\circ C$, whereas the acrylate ($R_1=H$) exhibits a color range at $57.8-59.2^\circ C$. A 1:1 mixture of the two exhibits a colored mesophase range of $56.5-55.9^\circ C$.

5 Secondly, combinations of similar monomers having very different alkylene chain lengths provide mixtures with substantially broadened mesophase ranges as compared to the individual components. For example, if a pair of acrylate monomers ($R_1=H$ and $y=0$) is prepared wherein one monomer has $A=-(CH_2)_{10}-$, and the other monomer has $A=-(CH_2)_3-$, the first monomer exhibits a color range of $57.8-59.2^\circ C$ whereas the second monomer exhibits no color. A 1:1 mixture of the two exhibits a 10 substantially broader color range of $68^\circ C$ to $-15^\circ C$, $-15^\circ C$ being the lower detection limit of the testing apparatus which was used. Accordingly, it will be seen that careful mixing of monomers can provide mesophases which exhibit full optical response over a variety of temperature ranges. 10

15 Thirdly, the addition of small amounts of non-mesogenic materials to a mixture of mesogenic materials can lead to substantial changes in the optical response ranges. Thus, for example, the addition of 2% of a photoinitiator or cross-linking agent can cause a downward shift of 10 degrees or 15 more in the color range exhibited by a mixture of the pure mesogenic materials.

As indicated above, an alternative method of preparing photopolymerized films having fixed optical properties is by combining a compound of the present invention with a second material which is suitable to permit formation of a film that exhibits cholesteric liquid crystalline properties. It is not 20 necessary that the second component be either polymerizable or mesogenic; nevertheless it is preferred that it be photopolymerizable in order to provide stable polymeric films. A wide variety of materials will be suitable to provide characteristic films. Examples of such materials, which are provided by way of illustration and not limitation, are cholesteryl oleyl carbonate and 2-methyl-1,4-phenylene-bis(4'-hexyloxybenzoate), which are mesogenic but not polymerizable; *p*-methoxyphenyl-*p*-25 (6-methacryloyloxyhexyloxy)benzoate, which is non-mesogenic but polymerizable; and cholesteryl 11-(methacrylamide)undecanoate, which is both mesogenic and polymerizable. Illustrations of the utility of certain of these compounds are provided in Example 9, below. 25

The color intensity and uniformity which may be shown by various combinations of the present invention will also be affected by the alignment. Thus, as is well known in the art, some form of 30 mechanical shearing must be provided to yield the colored films. Such alignment has been satisfactorily achieved by sandwiching the monomers between glass plates or polyester films. 30

Although polymerization of the films can be achieved by radical or thermal initiation, either in solution or in bulk, in virtually all instances, no fixed color or optical response is observed. Instead, the polymers formed in solution or in bulk tend to form colorless smectic mesophases or amorphous 35 polymers. Accordingly, photopolymerization is required to achieve the object of the present invention. The way in which photopolymerization is achieved may have an effect on the optical characteristics of the resulting polymer. Thus, where response duplication is desired, it appears desirable to use a high intensity light source which induces rapid polymerization. On the other hand, slower polymerization induced by lower intensity light may tend to produce polymeric films in which the response is shifted 40 toward the red end of the spectrum. 40

Multi-response films may also be produced according to the present invention by sequential photopolymerization of the unpolymerized films. For example, a colored film may be placed under a mask and irradiated to fix the color of the exposed areas. By removing the mask and changing the temperature of the partially cured film, a color change may be induced in the non-polymerized portion 45 of the film. Upon subsequent irradiation, the second color may be fixed, thereby providing a two-colored film. Of course, this technique may be extended to provide films having multiple optical responses, if desired by the artisan. 45

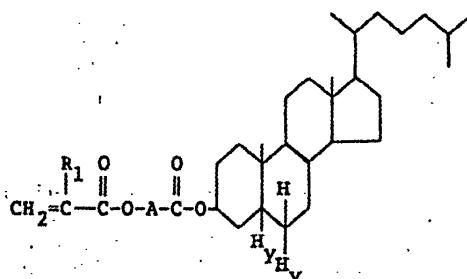
The unique ability of films of the present invention to reflect specific wavelengths of light varying from the near ultraviolet region into the infrared region makes them remarkably useful. For example, 50 their insensitivity to changes in temperature makes them especially suitable as filters, such as bandpass, notch, and circular polarization filters, in optical devices. Further, they will be well suited for use in reflective displays and so-called "Scheffer cells". In addition, where the films reflect in the visible spectrum and show bright iridescent colors, they will be useful as replacements for dyes and pigments. Thus, for example, they will be usable in floor and wall coverings, textiles, mats, paper products, and in 55 the graphic arts in nonconventional inks. 55

The advantages and attributes of the present invention will become more apparent from the following examples which are intended to illustrate but not to limit the scope of the present invention.

Examples

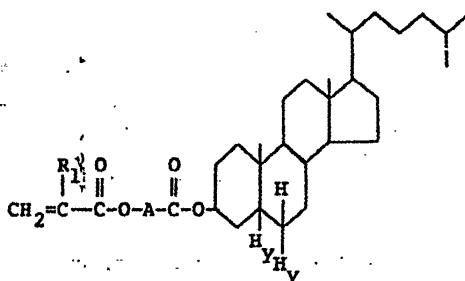
60 Compounds referred to herein by roman numeral designation have the following structures, the details of their preparation being described in our copending application referred to above. As used herein, the temperature ranges are melting ranges unless otherwise indicated by an asterisk (*) or by parentheses. An asterisk signifies that the range is a mesophase range whereas parentheses indicate that the range is a monotropic mesophase range, the latter being measured as the temperature is 60

decreased. With materials that have ascertainable melting ranges, the nonotropic mesophase range is often below the melting range.



where $A=R_1=O$ or $R_2=(CH_2)_n$

5	Compound	R_1	n	γ	Melting or mesophase range ($^{\circ}C$)	5
10	Va	H	10	0	*54.5—71.5	10
	Vb	CH ₃	10	0	*58—64	
	Vc	H	5	0	*45.5—68.5	
	Vd	CH ₃	5	0	*48.5—57.5	
	Ve	H	3	0	**68.5—70.5 (67.5)	
	Vf	CH ₃	3	0	73—74 (56.0)	
	Vg	H	3	1	41—43 (35.5)	
	Vh	CH ₃	3	1	43—45 (Below RT)	
15	Vi	H	10	1	62.5—64.5 (58.0)	15
	Vj	CH ₃	10	1	*33.7—49.0	



where $A=R_3O=(CH_2)_nO$, or
 $R_4O=(CH_2CH_2O)_n$

20	Compound	R_1	R_3O $(CH_2)_nO$	γ	Melting or mesophase range ($^{\circ}C$)	20
25	IXa	CH ₃	6	0	58.5—60 (51.0)	25
	IXb	CH ₃	2	0	80—81 (40.1)	
	IXc	H	2	0	85.5—87 (56.0)	
	IXd	H	6	0	*52—62	
			R_4O $(CH_2CH_2O)_n$			
	IXe	CH ₃	2	0	48.5—52.9 (33.1)	
	IXf	CH ₃	3	0	no m. pt. (6.5)	

30 Example 1

This example sets forth the color ranges of various monomeric esters V described above, measured with a L. itz optical microscope using transmitted light. A Mettler FP5 temperature regulator and a Mettler FP52 hot stage were used to control the temperature, cooling being obtained by passing a nitrogen stream through a dry-ice cooled copper coil and, subsequently, the FP52.

		Compound	Color range (°C)	
5	Va	57.8—59.2		
	Vb	(55.8—55.3)		
	Vc	(48.5—33.0)		
	Vd	(51.0—26.5)		5
	Ve	No color		
	Vf	No color		

Example 2

This example describes the colored mesophase ranges obtained for mixtures of previously described paired monomers having identical alkyl chain lengths.

The measurements were made using the apparatus described in Example 1, by heating a mixture of the monomers to a melt and cooling. The components were 1:1 mixtures by weight.

15	Components	R_2 or R_3O		Optical response range (°C)	15
		n	Color range		
20	Va—Vb	10	Violet—Red	(56.5—55.9)	
	Vc—Vd	5	Violet—Orange	(50.2—29.5)	
	Ve—Vf	3	No color	61.5 Mesophase	
	Vg—Vh	3	No color	Not Measured	
	Ixa—IxD	6	Violet—Blue Violet	(51—1)	20
	IXb—IXc	2	No color	47 Mesophase	

Example 3

This example describes the colored mesophase ranges obtained for two-component mixtures of previously described monomers having different alkyl chain lengths. Color measurements were made as described in Example 1. The components were 1:1 mixtures by weight.

	Components	R_2 or R_3O		Optical response range (°C)**	30
		n	Color range		
30	Va	10	Violet—Orange Red	68.0—15)	
	Ve	3			
	Vb	10	Green—Orange	(47.5—15)	
	IXc	2			

**—15°C is the lower temperature limit of the thermostated water bath.

Example 4

This example describes the colored mesophase ranges for mixtures of previously described monomers having different alkyl chain lengths. The mixtures comprised Irgacure 651 photoinitiator and, optionally, other indicated components. Irgacure 651 is 2,2-dimethoxy-2-phenyl acetophenone. Color measurements were made using a thermostated water bath.

40	Components	Wt. (g)	Optical response range (°C)		40
			Color range		
45	Vb	1.0			
	Ve	1.0	Violet—Red	(50—5)	
	Photoinitiator	0.04			
	Vb	0.25			
	Vh	0.25	Blue Green—Red	(40—5)	45
	Photoinitiator	0.01			
50	Vd	0.50			
	Vf	0.50	Green—Red	(45—30)	
	Photoinitiator	0.02			
	Vb	0.50			
	IXb	0.50			

	<i>Components</i>	<i>Wt. (g)</i>	<i>Color range</i>	<i>Optical response range (°C)</i>	
5	Photoinitiator	0.02	Orange Green—Red	(32—0)	5
	Methylmethacrylate	0.05			
	Vd	0.40			
	Vc	0.40			
	Va	0.20	Violet—Orange	(16—6)	
10	Photoinitiator	0.02			10
	Trimethylolpropane-triacrylate	0.06			
	Vb	0.5			
	IXe	0.5	Green—Red	(37—0)	
	Photoinitiator	0.01			

15 **Example 5**

This example illustrates a colored polymeric film derived from a film comprising a single monomer of the present invention and 1% Irgacure 651 photoinitiator. The table lists "apparent absorbance" maximum (λ max), percentage transmittance (%T) and half-width at half-height (HW-HH) of the film and the resulting polymer when the film was photopolymerized at an indicated temperature.

20 The polymerizations in this and other examples were achieved by exposing the film to a 450-watt mercury arc lamp for about 30 seconds.

25	<i>Component</i>	<i>Film Temp. (°C)</i>	<i>Monomeric film</i>			<i>Polymer</i>			25
			λ max (nm)	%T	HW-HH (nm)	λ max (nm)	%T	HW-HH (nm)	
	Vg	25	738	53	45	738	55	50	
	IXd	25	438	49	27	441	46	33	

Example 6

This examples illustrates several colored polymeric films derived from indicated monomer compositions. All films contained 1% Irgacure 651 Photoinitiator. Also, four of the films contained 3% trimethylolpropane triacrylate, while pair Vb:IXb contained 3% trimethylolpropane trimethacrylate.

35	<i>Composition (by weight)</i>	<i>Film Temp. (°C)</i>	<i>Monomeric film</i>			<i>Polymer</i>			35
			λ max (nm)	%T	HW-HH (nm)	λ max (nm)	%T	HW-HH (nm)	
	Va:Ve (1:1)	23	505	49	18	505	51	20	
	Vb:IXb (1:1)	25.5	585	42	21	585	42	21	
	Vc:IXc (3:1)	25.5	563	46	25	568	45	26	
40	Vc:IXc* (1:1)	24.5	950	53	50	950	53	50	40
	IXc:IXd* (1:1)	25.5	1260	59	112	1260	59	112	

* Colorless mixture

Example 7

This example illustrates the differently colored polymeric films which may be produced by subjecting a monomeric mixture to different temperatures and then exposing the colored film to UV radiation. The monomeric mixture described for this example comprises a 1:1 by weight mixture of compounds Vb and Vf. The apparent absorbance maximum and color are reported for each film.

	<i>Film temperature (°C)</i>	λ max (nm)	<i>Color</i>	
50	45	485—470	Blue—Green	50
	35	515	Green	
	25	542	Lime Green	
	11	605	Orange	

A comparable experiment conducted with a 1:1 mixture of compounds Va and Vf gave the following results:

	<i>Film Temp. (°C)</i>	<i>λ max (nm)</i>	<i>Transmittance (%)</i>	<i>HW-HH (nm)</i>	<i>Color</i>	
5	32	480	47	32	Blue	5
	23	505	51	20	Blue-Green	
	18	530	48	42	Lime-Green	
	10	574	48	40	Orange	

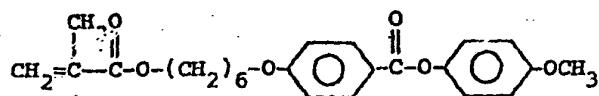
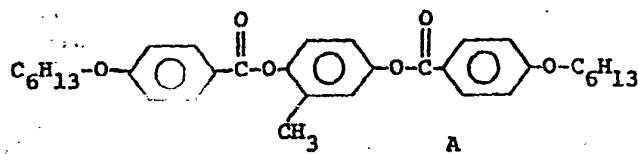
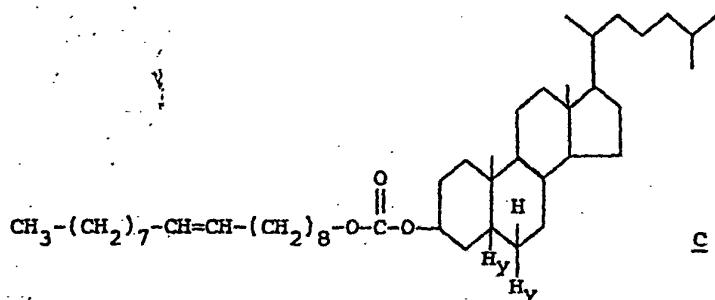
Example 8

This example illustrates the effect of non-mesogenic materials on a mixture of monomers. A 1:1 by weight mixture of compounds Vc and Vd gave a colored mesophase range of 50.2—29.5°C, as indicated in Example 2. When 2% by weight of photoinitiator was added, the colored mesogenic range shifted to 43—20°C.

Example 9

This example illustrates polymer films which can be prepared from a compound of the present invention and unrelated materials, as follows:

15

**B**

Compound A is a nematic liquid crystalline material which is not capable of participating in a photopolymerization reaction. Compound B is a nonmesogenic material that is capable of participating in a photopolymerization reaction. Compound C is a cholesteric liquid crystalline material which is not capable of participating in a photopolymerization reaction. All three are suitable to permit formation of a film that exhibits cholesteric liquid crystalline properties. To illustrate this, films were prepared and photopolymerized using 1% Irgacure 651 photoinitiator and 3% trimethylolpropane trimethacrylate.

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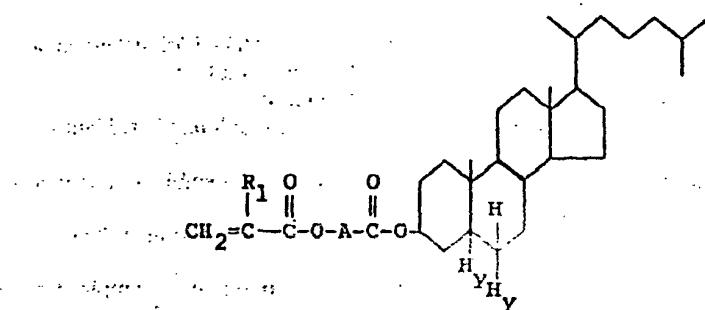
25	<i>Composition (weight ratio)</i>	<i>Film Temp. (°C)</i>	<i>Monomeric film</i>			<i>Polymer</i>			25
			<i>λ max (nm)</i>	<i>%T</i>	<i>HW-HH (nm)</i>	<i>λ max (nm)</i>	<i>%T</i>	<i>HW-HH (nm)</i>	
30	Vd:A (2:1)	24	355	43	30	350	41	35	30
	Vb:B (1:1)	25	388	52	15	400	42	40	
	Vg:C (4:1)	25	700	51	33	730	55	52	

Although the film derived from pair Vd:A demonstrates suitable optical properties, it is not as stable as other films in which both members of the pair are polymerizable. For example, when this

polymeric film was heated at 60°C for one day, it underwent crystallization to give an opaque colorless film.

Claims

1. A composition suitable to provide a polymeric film having a fixed optical response, said composition comprising:



where $R_1=H$ or CH_3 , $A=-R_2-$, $=R_3O$, or $=R_4O-$, R_2 =an alkylene chain having 3-14 methylene or lower alkyl-substituted methylene groups, R_3 =an alkylene chain having from 2-14 methylene or

10 lower alkyl-substituted methylene groups, R_3 =an alkylene chain having from 2-14 methylene or lower alkyl-substituted methylene groups, R_4 =an alkylene ether, diether or triether having a total of from 3-14 carbon atoms in the alkylene linkages, provided that the terminal alkylene linkage adjacent to the carbonate moiety comprises not less than two carbon atoms and $y=0$ or 1; and a photoinitiator.

15 2. A composition as claimed in claim 1, wherein said composition comprises a second material which is suitable to permit formation of a film that exhibits cholesteric liquid crystalline properties.

16 3. A composition as claimed in claim 2, wherein said second material is a compound of the formula I.

17 4. A composition as claimed in claim 2, wherein said second material is a photopolymerizable material having a structure other than that of formula I.

18 5. A composition as claimed in claim 2, wherein said second material is a mesogenic material having a structure other than that of formula I.

19 6. A composition as claimed in any one of claims 1 to 5, wherein said composition comprises a crosslinking agent.

20 7. A composition as claimed in any one of claims 1 to 6, wherein the or at least one of the compounds of formula I contains an R_4 group and wherein at least one of the alkylene linkages thereof is branched, the or each branch containing up to 4 carbon atoms.

21 8. A polymeric film having a fixed optical response, said film being obtained by photopolymerizing a composition comprising a photopolymerizable monomer of the formula I and a photoinitiator.

22 9. A film as claimed in claim 8, wherein said composition also comprises a second material which is suitable to permit formation of a film that exhibits cholesteric liquid crystalline properties.

23 10. A film as claimed in claim 9, wherein said second material is a compound of the formula I.

24 11. A film as claimed in claim 9, wherein said second material is a photopolymerizable material having a structure other than that of formula I.

25 12. A film as claimed in claim 9, wherein said second material is a mesogenic material having a structure other than that of formula I.

26 13. A film as claimed in any one of claims 9 to 12, wherein said composition comprises a crosslinking agent.

27 14. A film as claimed in any one of claims 8 to 13, wherein the or at least one of the compounds of formula I contains an R_4 group and wherein at least one of the linkages thereof is branched, the or each branch containing up to 4 carbon atoms.

28 15. A film as claimed in any one of claims 8 to 14, which is colored.

29 16. A film as claimed in claim 15 which comprises multiple colors.

30 17. A film as claimed in any one of claims 8 to 16, which reflects ultraviolet light.

31 18. A film as claimed in any one of claims 8 to 17, which reflects infrared light.

32 19. A process for preparing a film comprising a polymeric liquid crystalline material having a fixed optical response, said process comprising the steps of preparing a film comprising a photopolymerizable monomer of the formula I, and a photoinitiator; aligning said film; adjusting the temperature of said film to obtain a desired optical response; and photopolymerizing said film.

33 20. A process as claimed in claim 19, wherein said film comprises a second material which is suitable to permit formation of a film that exhibits cholesteric liquid crystalline properties.

34 21. A process as claimed in claim 20, wherein said second material is a compound of the formula I.

22. A process as claimed in claim 20, wherein said second material is a photopolymerizable material having a structure other than that of formula I.

23. A process as claimed in claim 20, wherein said second material is a mesogenic material having a structure other than that of formula I.

5 24. A process as claimed in any one of claims 19 to 23, wherein said composition comprises a crosslinking agent. 5

25. A process as claimed in any one of claims 19 to 24, wherein the or at least one of the compounds of formula I contains an R_4 group and wherein at least one of the alkylene linkages thereof is branched, the or each branch containing up to 4 carbon atoms.

10 26. A process as claimed in any one of claims 19 to 25 comprising the additional steps of masking at least a portion of said film from the photopolymerizing radiation, removing said mask upon completion of the photopolymerization, adjusting the temperature of said film such that the unpolymerized regions of said film exhibit a different optical property, and 10

15 photopolymerizing said film, thereby providing a polymeric film which exhibits multiple optical properties. 15

27. A composition as claimed in claim 1, substantially as described in any one of the examples herein.

28. A film as claimed in claim 8, substantially as described in any one of the examples herein.

20 29. A process as claimed in claim 19, substantially as described in any one of examples herein.

30. The photopolymerization product of the composition defined in any one of claims 1 to 7.

31. Any new composition, material, film, process or product hereinbefore described. 20

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1984. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.